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Michael R. Korn, Ron J. Pieper and Jianmin Shi

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Department of Electrical Engineering,
University of Texas at Tyler
3900 University Blvd.
Tyler, TX 75799

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9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)

Dr. Eric Forsythe (office phone 301 394-0606)
U.S. Army Research Laboratory
AttN: AMSRD_ARL-SE-EE
2800 Powder Mill Road
Adelphi, MD 20773-1197

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Increased Coplanarity and Conjugation and Lowered HOMO-LUMO Energy Differences in Benzochalogens Connected to Aromatic Substituents via Ethynyl Spacers: A DFT Study The simple insertion of an ethynyl spacer between aromatic substituents and benzochalogen cores significantly increases coplanarity and decreases HOMO-LUMO energy differences by up to 30% when compared to the corresponding compounds without the ethynyl spacer as determined by DFT analysis. This concept also applies for oligomers.

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Increased coplanarity and conjugation and lowered HOMO-LUMO energy differences in benzochalogens connected to aromatic substituents via ethynyl spacers: A DFT study

Michael R. Korn[*] *Ron Pieper,*[†¶] *Jianmin Shi*[‡]

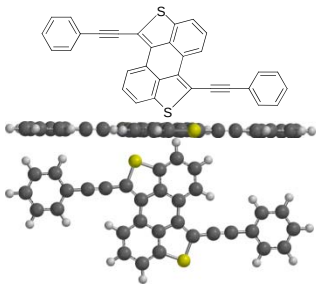
Chemistry Department Liberty University, Lynchburg Virginia[*],The University of Texas at Tyler, [¶]Department of Electrical Engineering, Tyler, TX 75799; [‡]U.S. Army Research Laboratory, Adelphi, MD 20783. *Corresponding author. E-mail: rpieper@uttyler.edu.

DFT calculations on the B3LYP/6-31G* level were performed for organic semiconductors based on benzochalcogens (bibenzodithiophenes, naphthodithiophenes, bibenzodiselenophenes) bearing lateral aromatic substituents (phenyl, thienyl, naphthyl, pyrenyl). Direct attachment of these aromatic substituents to the benzochalcogen core resulted in non-coplanar geometries due to steric interactions between the core and the lateral aromatic groups. However, when utilizing an ethynyl moiety as a spacer between core and aromatic substituent, coplanarization and up to 30% reduction in HOMO-LUMO energy differences (gap energies) were achieved. This concept was also successfully extended to bibenzothiophene-based oligomers.

Michael R. Korn*, Ron Pieper and Jianmin Shi

Increased Coplanarity and Conjugation and Lowered HOMO-LUMO Energy Differences in Benzochalogens Connected to Aromatic Substituents via Ethynyl Spacers: A DFT Study

The simple insertion of an ethynyl spacer between aromatic substituents and benzochalogen cores significantly increases coplanarity and decreases HOMO-LUMO energy differences by up to 30% when compared to the corresponding compounds without the ethynyl spacer as determined by DFT analysis. This concept also applies for oligomers.



Introduction

Organic semiconductors have gained an appreciable amount of significance in applications for organic thin film transistors (OTFTs)[1] and solar cells[2] over the past decade. Increasing efforts in device design, the selection of suitable device materials, and the synthesis of novel organic materials with improved electrical properties have considerably advanced the field and led to devices with mobilities of up to 5 cm^2/Vs or higher.[3] The ongoing need for organic molecules with superior electrical properties has produced a large variety of novel organic compounds[4] most of which are based on extended π-systems derived from phenyl rings, thienyl rings, or combinations of the same, thus constituting the classes of acenes, thiophenes, and benzothiophens, respectively. Of particular interest in devising new molecules is the extent of conjugation as it directly determines the HOMO-LUMO energy gap, E_g. To efficiently contribute to the delocalization of electrons, maximum overlap of the contributing orbitals within the compound is required which is achieved if the molecule adopts a coplanar geometry. However, steric repulsion of neighboring rings might prevent coplanarization and thus will result in higher E_gs than expected. Here, we like to report on the effectiveness of the ethynyl (acetylide) group when utilized as a spacer to link neighboring aromatic units in selected organic semiconductors to bring about significantly lowered energy gaps and increased coplanarity as assayed by DFT calculations. DFT has been reported as a suitable tool for modeling organic semiconductors using the B3LYP functional in combination with various basis sets. Examples include the following compounds (with their DFT method listed in parentheses): dinaphtho[2,3-*b*:2'3'-*f*]thieno[2,3-*b*]-thiophene (B3LYP/6-31G(d,p) among others),[5] tetraceno[2,3-*c*]thiophenes (B3LYP/6-31G**),[6] (indeno)fluorine-triphenylamine copolymers (B3LYP/6-31G*),[7] phenothiazines (B3LYP/6-31G*),[8] fullerenes (B3LYP/3-21G*),[9] tetraceno[2,3-*b*]thiophenes (B3LYP/D95(d)+),[10] a functionalized triarylamine for dye-sensitized solar cells (B3LYP/6-31+G(d)),[11] and arylene diimides (B3LYP/6-31G*),[12] (B3LYP/6-31G**).[13] The ethynyl group is particularly suited as a spacer because of its linearity, absence of sterically demanding atoms,

absence of *cis*/*trans* isomerizations, ability to participate in conjugation, and some well-established synthetic methods for its incorporation.[14] The ethynyl moiety has previously been reported as part of the chemical structure in some organic semiconductors, including 6,13-bis(triisopropylsilylethynyl)-pentacene in which the oxidatively instable 6, 13 positions of pentacene are stabilized by the TIPS groups which also increase pentacene's solubility,[15] in molecules representing subunits of graphyne,[16] in liquid crystalline alkylthienyl thiophenes,[17] in phenothiazine-based[18] and thienyl and phenyl-based[19] thiols for monolayers, and in derivatives of 3,4:3',4'-bibenzo[*b*]thiophene (BBT) **1**;[20] yet, its deliberate use as a suitable structural unit for coplanarization in those and other organic semiconductors has not been fully appreciated.

The particular class of organic semiconductors that initiated our research is based on BBT. The synthesis of BBT was first reported by Wudl *et al.* in 1979 and reported by the same authors to conduct electricity when doped with iodine.[21] However, for almost four decades this molecule lost attention until two research groups very recently published BBT-based compounds as organic semiconductors.[20, 22] One of the groups reported mobilities of about 0.35 cm^2/Vs, on/off ratios of 2×10^5, and good shelf life for devices made from several BBT-derived compounds.[22] A significant number of the compounds reported in both publications were BBT derivatives in which an aromatic group was directly attached to the BBT core. No experimental data or theoretical calculations of E_g for any of those compounds are reported in the current literature. Our initial DFT calculations of HOMO and LUMO energies showed only insignificant differences in E_g between BBT and such BBT derivatives to which the aromatic group was directly attached. This was somewhat surprising, as the laterally attached aromatic groups provide a substantial number of additional delocalized electrons in potential conjugation with the BBT core and thus should give rise to a notably reduced E_g. Molecular modeling of those compounds however showed that the aromatic groups were not coplanar with the BBT core. The improved design of modified BBT molecules with the ethynyl unit as a spacer between the BBT core and the aromatic ring afforded coplanarity, and significantly lowered energy gaps were observed. To test the extent of this concept of employing an ethynyl spacer in organic semiconductors, DFT calculations were not only performed for

the aforementioned BBT-based compounds but also for the corresponding bisbenzoselenophenes, for naphthodithiophenes, and for BBT-based oligomers.

Experimental Section

DFT calculations were performed on the B3LYP/6-31G* level using the SPARTAN 08 software provided by Wavefunction, Inc. Irvine, CA. Structures were drawn using SPARTAN software, typically minimized (molecular mechanics), and submitted for analysis. Rotational barriers were calculated with DFT on the B3LYP/6-31G* level by drawing the molecule with SPARTAN software, specifying the dihedral plane, rotation angle, and increments of rotation and then submitting for calculation.

Results and Discussion

Benzodithiophenes. HOMO/LUMO energy levels, and therefrom E_g = |HOMO – LUMO|, were determined by DFT calculations for several BBT derivatives in which a phenyl (**2**), 2-naphthyl (**3**), 1-pyrenyl (**4**), or 2-thienyl (**5**) ring was directly attached at the 1,7 positions of the BBT core. DFT results are summarized in Table 1. DFT calculations for reference compounds BBT (**1**), pentacene (**6**) and 6-αT (**7**) are listed in Table 2. The structures of molecules **1-7** are shown in Figure 1.

Table 1. HOMO/LUMO Energy Levels E_g^{no} for Molecules **2-5** Based on DFT Calculations (B3LYP/6-31* Level)

	HOMO [eV]	LUMO [eV]	E_g^{no} [eV]
2	-4.99	-1.40	3.59
3	-4.93	-1.35	3.58
4	-5.00	-1.71	3.29
5	-5.10	-1.75	3.35

Table 2. HOMO/LUMO Energy Levels E_g for Reference Molecules 1, 6-7. E_g^{exp} Provides Experimental Data from the Literature

	HOMO [eV] [a]	LUMO [eV] [a]	E_g [eV] [a]	E_g^{exp} [eV]
BBT, 1	-5.14	-1.53	3.61	n/a
Pentacene, 6	-4.60	-2.39	2.21	1.82[23]
				1.86[24]
				> 2.2[25]
α-6T, 7	-4.80	-2.18	2.62	2.2[26]
				2.3[27]
				3.0[28]

a: Based on DFT calculations (B3LYP/6-31* level).

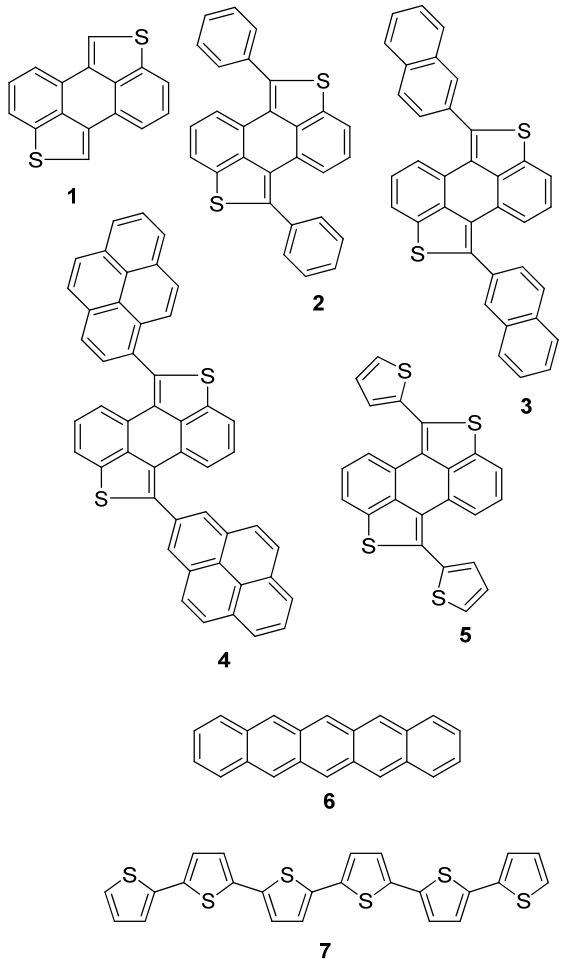


Figure 1. Molecules **2-5** with aromatic groups directly attached to BBT (**1**); pentacene (**6**), and α-6T (**7**).

DFT calculations of energy gaps for BBT-based molecules **2-5** with no spacer (E_g^{no}) are basically unaffected (**2, 3**) or only slightly reduced (**4, 5**) when compared to E_g of the parent BBT molecule **1** (Tab. 2), and they are 1.0 – 1.4 eV higher than E_g for pentacene or α-6T. A closer look at the minimized energy conformation of compounds **2-5** reveals that in all cases the laterally attached substituents are not coplanar with the BBT core but rather are rotated out of plane by 60°, 58°, 80°, and 55°, respectively, as exemplarily shown in Figure 2 for **2**. This non-coplanarity significantly reduces overlap of p-orbitals between the aromatic substituent and the BBT core as pictured in the graphical representation of the corresponding HOMO wave function for **2** (Figure 2b). As can be seen, the HOMO is almost completely restricted to the BBT core with little contribution from the lateral aromatic ring.

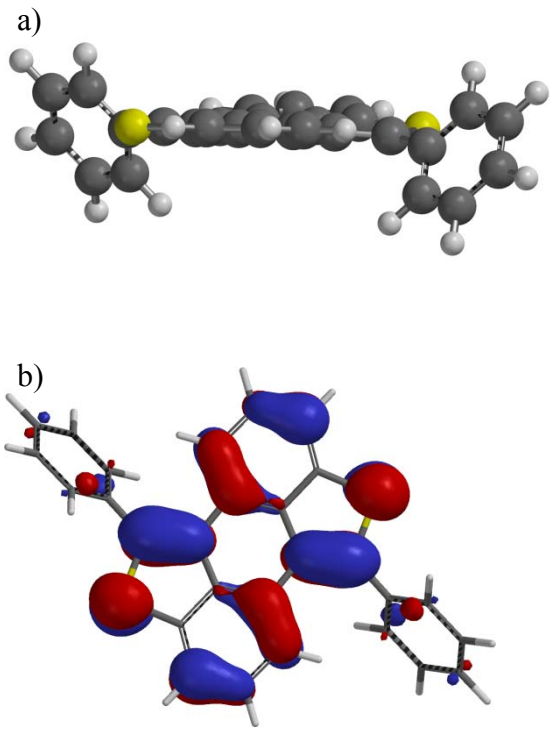


Figure 2. (a) Minimized structure of BBT derivative **2**; (b) HOMO wave function of **2**.

The main reason as to why the aromatic substituents in 2,7-position rotate out of plane is because of steric strain imposed upon the system by interactions of the hydrogen atoms in *ortho* position of the lateral aromatic substituent with the hydrogen atoms at the 3 and 8 positions of the BBT core. Because the interacting hydrogen atoms are located on two C atoms that are separated by four additional C atoms, one could refer to a 1,6 steric interaction. The extent of this 1,6 steric interaction was investigated for the mono-substituted analogue of **2**, compound **8**, which bears only one laterally attached phenyl ring (Figure 3). DFT calculations of the rotational barrier around the bond that connects the phenyl substituent with the BBT core in **8** (bolded bond in Fig. 3) result in 65kJ/mol for dihedral angles between 0 and 70° and a pointed gain in energy stabilization for (close to) orthogonal (90°) conformational geometries (Fig. 3). This high energy barrier explains the energetically preferred non-coplanar geometry as observed in DFT calculations for compounds **2**-**5**.

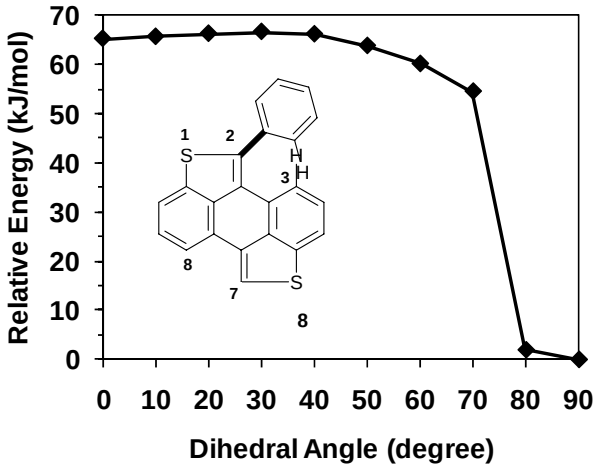


Figure 3. Energy profile (B3LYP/6-31G* level) from coplanar to orthogonal geometry of a laterally attached phenyl ring in substituted BBT molecule **8**; the bolded line in the structure of **8** indicates the bond around which the phenyl substituent is rotated to generate the energy profile shown.

To alleviate steric strain in molecules **2**-**5**, acetylide groups were employed as spacers in the 2 and 7 positions of **1** to give compound **9** and there from molecules **10 - 13** (Figure 4) (compound **10** was also listed in ref. 20, however without commenting on the implication of this spacer). DFT calculations of

HOMO/LUMO energies and energy gaps for compounds **9-13** bearing the triple bond (E_g^t) are listed in Table 3.

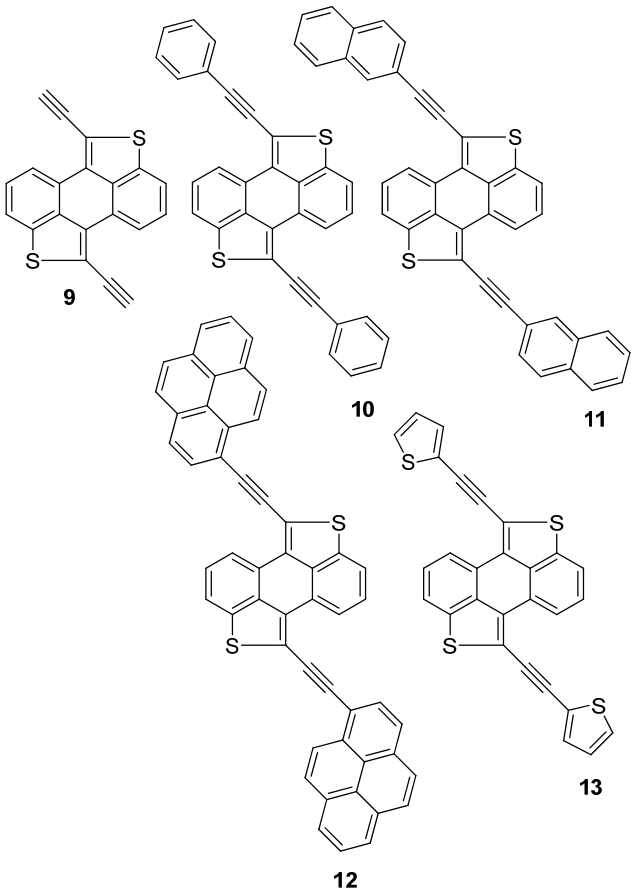


Figure 4. Structure of BBT compounds **9-13** with ethynyl groups.

Table 3. HOMO/LUMO Energy Levels and E_g^t for BBT-based Molecules 9-13

	HOMO [eV]	LUMO [eV]	E_g^t [eV]	Net change of E_g [eV (%)[a]]		Contribution to E_g^t from increased conjugation based on E_g^{no} [eV] [b]	Energy-minimized dihedral angle
				Calculated based on E_g^{BBT}	Calculated based on respective E_g^{no}		
9	-5.20	-2.18	3.02	-0.59 (-16%)	n/a	0	n/a
10	-4.95	-2.29	2.66	-0.95 (-26%)	-0.93 (-26%)	-0.34	0°

11	-4.92	-2.32	2.60	-1.01 (-28%)	-0.98 (-27%)	-0.39	2°
12	-4.80	-2.46	2.34	-1.27 (-35%)	-0.95 (-29%)	-0.36	5° [c]
13	-4.91	-2.35	2.56	-1.05 (-30%)	-0.79 (-24%)	-0.20	0°

a: Calculated as (E_g^t / E_g^{BBT} or E_g^{no}) -1 x 100. b: Based on respective compound without spacer: calculated as ($E_g^{no} - E_g^t + 0.59$ eV) / ($E_g^{no} - E_g^t$). c: DFT calculations of rotational barriers between the BBT core and the 2-pyrenyl side group show another energy minimum at about 30° which lies 0.1 kJ/mol lower than the 0° conformation (see supporting information).

Overall, gap energies for compounds **10-13** are lowered by as much as 1.27 eV (35%) when compared to the non-substituted BBT core **1** ($E_g^{BBT} - E_g^t$) and by up to 0.95 eV (29%) when compared to their respective counterparts **2-5** ($E_g^{no} - E_g^t$). About 0.6 eV of reduction in gap energy can be attributed to the presence of just the two acetylene spacers (compound **9**). The same amount of reduction in gap energy is obtained from DFT calculations of **10** when setting the phenyl ring purposefully to 90° (E_g = 3.01 eV). Employing 0.6 eV as the basic value of reduction for all four compounds **10-13**, the reduction in E_g^t due to increased conjugation from the lateral aromatic groups because of the relief of steric strain comes out to about 0.20 – 0.39 eV (Tab. 3). DFT results in Tab. 3 also show that the lowering of gap energies is primarily due to a lowered LUMO which will have some implications on device design (***e.g.*** the selection of electrodes with suitable work functions) and on oxidative stability. Energy-minimized conformations of compounds **10-13** now exhibit dihedral angles of 0°- 5° and rotational barriers between the BBT core and the lateral substituent of 3.5 – 5.5 kJ/mol (see supporting information for rotational energy profiles of mono-substituted analogues of **10-13**). Figure 5 shows the energy minimized conformation of compound **10** (top (a) and side (b) view), now being coplanar, and its HOMO wave function (Fig. 5 (c)). The HOMO receives a significant contribution from the ethynyl spacers and a larger - when compared with its orthogonal geometry - contribution from the lateral coplanar phenyl group.

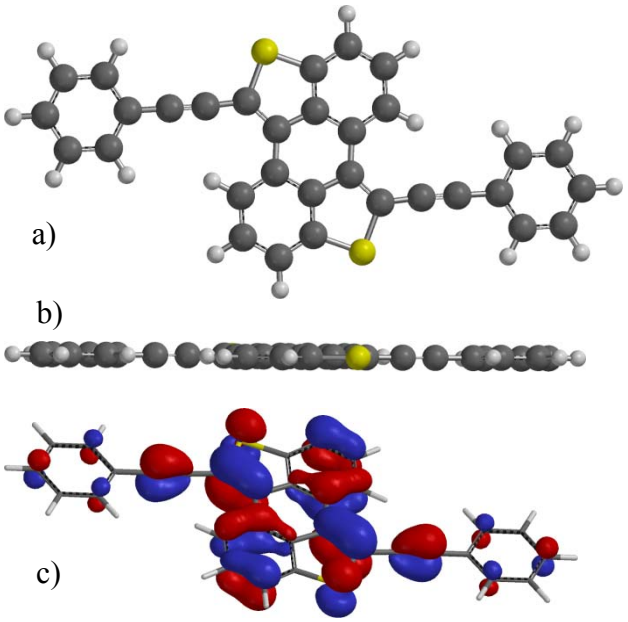


Figure 5. Minimized geometry for **10**; (a) top view; (b) side view; (c) HOMO of **10**.

The effect of the ethynyl group in BBT derivatives was compared with the effect of two other spacers, namely the *trans*-C,C double bond and the ethylene -CH_2-CH_2- single bond group (compounds **14** and **15**, respectively in Figure 6). DFT calculations for **14** result in E_g^d (energy gap for compounds with double bond spacers) = 2.73 eV (24 % reduction based on E_g^{no} for **2**) and for **15** in E_g^s (energy gap for compounds with single bond spacers) = 3.56 eV (less than 1% change when compared to **2**). The minimized structure for **14** (supplemental information) shows that both the *trans* double bond as well as the phenyl ring are tilted out of plane, resulting in an overall dihedral angle of about 40° between the BBT core and the lateral phenyl rings. When both spacers are employed in the corresponding BBT thienyl derivatives, similar results are obtained (E_g^d = 2.69 eV, dihedral angle = 37°; E_g^s = 3.55 eV). The *trans* double bond is thus capable of reducing E_g to a similar extent as the triple bond, yet, falls short of coplanarizing the respective BBT derivatives. The single-bond -CH_2-CH_2- spacer, even though it spaces the phenyl ring away from the core, is ineffective in lowering E_g as it does not provide conjugation between the core and the lateral aromatic rings.

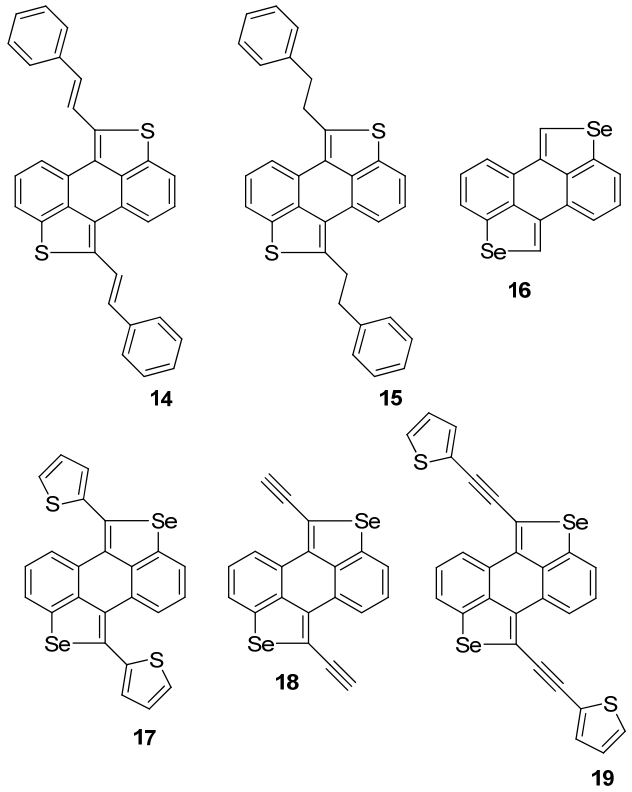


Figure 6. BBT derivatives with *trans*-CH=CH- and the $–CH_2-CH_2-$ spacer (**14**, **15**); compounds based on BBSe (**16-19**)

Bisbenzoselenophenes. Substituting the sulfur atoms in BBT by the next higher chalogen, selenium, leads to BBSe **16** (Figure 6). E_g for **16** obtained from DFT calculations give 3.45 eV (HOMO: -5.09 eV; LUMO: -1.54 eV). Attaching a lateral thienyl group to BBSe gives **17** with E_g^{no} = 3.26 eV (dihedral angle of about 70° and twisted BBSe core of about 5-10° out of plane). BBSe with two acetylene groups **18** yields E_g^{t} = 2.86 eV (17 % reduction of E_g). Linking the thienyl group to BBSe via acetylene spacers (compound **19**) results in a further lowering to E_g to E_g^{t} = 2.51 eV (23 % reduction in E_g based on **17**; dihedral angle of 0°). The effect of the ethynyl spacer for BBSe thus parallels the effect of what is observed for BBT.

Napthodithiophenes. The concept of employing an ethynyl spacer was applied to derivatives of the corresponding naphthodithiophenes (NDTs), based on the respective core **20** (HOMO: -4.98 eV; LUMO: -1.87 eV; E_g: 3.11 eV) (Figure 7). Direct attachment of a thienyl substituent at positions 2 and 7 gives **21**, a compound reported by Takimiya *et al.*[29] The reported single crystal XRD of **21** showed

that the resulting geometry was 'nearly planar'; the highest wavelength in the published UVvis spectrum for **21** (in THF) was 518 nm (2.39 eV). These data were compared with our DFT calculations which gave a dihedral angle of 25° and an energy gap E_g^{no} of 2.32 eV. Following the same protocol as for BBT and BBSe, NDT with just the acetylene spacers was modeled (compound **22**) resulting in E_g = 2.54 eV, a 18% reduction in E_g and thus very similar to the effect observed for BBT- and BBSe-based molecules. When linking the NDT core and the thiophene substituent *via* the ethynyl spacers (compound **23**) coplanarity and E_g^{t} = 1.88 eV are achieved (a 19% reduction in E_g based on E_g for **21**; a 40% reduction when based on **20**).

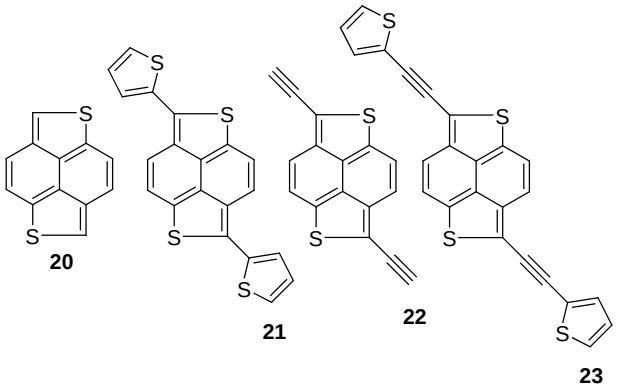


Figure 7. Naphthodithiophene-based compounds **20-23**.

Oligomers. The concept of bridging core and aromatic substituents by an ethynyl unit was further extended to oligomers. Compound **24** comprises BBT cores linked to thiophene units via ethynyl spacers as depicted in Figure 8. n-Hexyl groups, utilized in oligothiophenes to increase solubility,[30] were added in 3-position on the bridging and terminal thiophene rings of **24** to give **25**. BBT oligomers **26** without the ethynyl bridging units were investigated as well. DFT calculations for E_g based on the respective number of repeating units are shown in Figure 9. E_g decreases asymptotically from 2.5 eV to values of 2.0 eV or less within only a few repeating units for the two oligomers that employ the ethynyl spacer. This holds true regardless of whether or not a hexyl group is present, allowing for alkyl-substituted BBT-based oligomers with improved solubilities without compromising low energy gaps.

Energy gaps for BBT units directly linked via thienyl units (**26**) also decrease by about 0.4 eV to 2.9 eV (tetramer), yet are offset by about 1 eV towards higher energies.

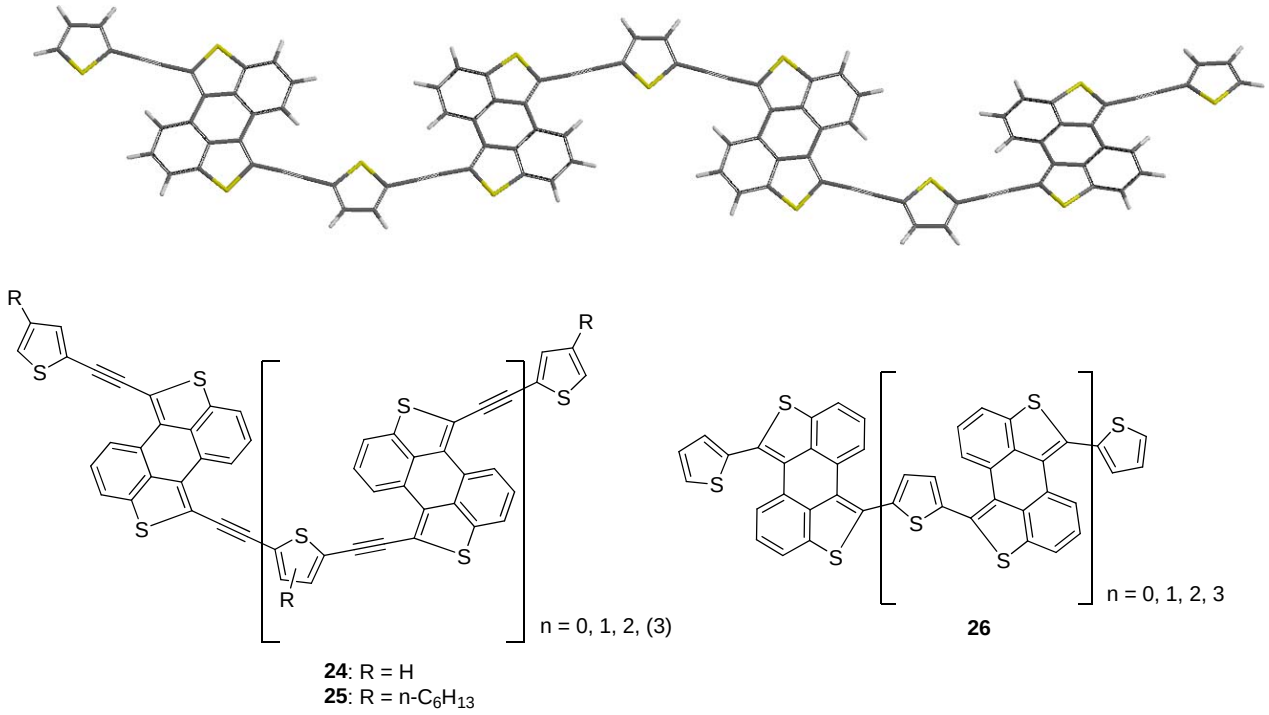


Figure 8. Minimized geometry of tetramer for **24** (top) and general structure of oligomers **24**, **25**, and **26**.

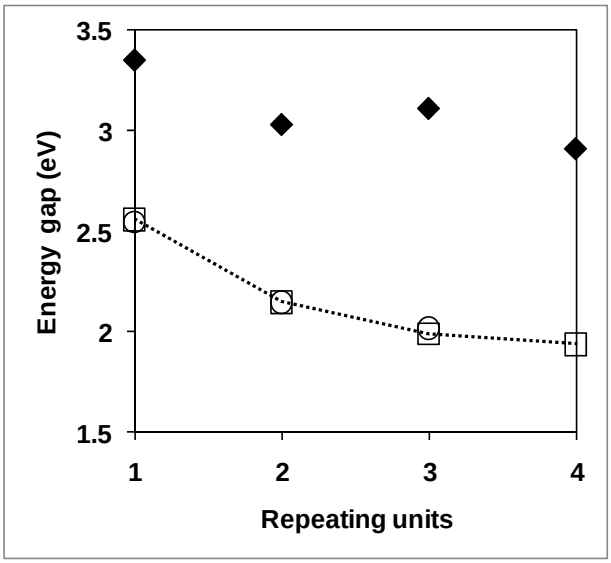


Figure 9. Gap energies for oligomers **24** (open squares), **25** (open circles), and **26** (diamonds) dependent on degree of oligomerization; the dashed line is added as a visual aide.

Conclusions

HOMO/LUMO energy levels and gap energies E_g were calculated for a variety of novel benzochalogens by DFT calculations. Utilizing the ethynyl spacer as a bridging unit between the aromatic core and laterally attached aromatic substituents results in a 20-30% lowering of gap energies. The two main contributions to this lowering of E_g stem from the additional π-electrons provided by the acetylene unit and from favored coplanarization of the lateral aromatic substituents. This concept also applies to oligomers. These studies show that increasing coplanarity while maintaining conjugation through a suitable spacer such as the ethynyl unit, can significantly lower energy gaps in organic semiconductors. Applying this concept to the synthesis of new molecules or to the redesign of already existing chemical systems can result in organic semiconductor materials with improved properties for electrical device designs.

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Supporting Information Available: Energy-minimized structures of compounds **2**-**5**, **10**-**15**, **17**, **19**, **21**, **23**, **26**. Rotational energy profiles for mono-substituted analogues of compounds **10**-**13**. This material is available free of charge via the Internet at http://pubs.acs.org.

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